Neutron Studies of the Iron-based Family of High Tc Magnetic Superconductors

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ABSTRACT

We briefly review recent neutron scattering investigations carried out at the NIST Center for Neutron Research on the crystal structures, magnetic structures, and spin dynamics of the iron-based *R*OFe(As,P) (*R*=La, Ce, Pr, Nd), and (Ba,Sr,Ca)Fe_2As_2 systems. All the undoped materials exhibit universal behavior, where a tetragonal-to-orthorhombic structural transition occurs between ~100-220 K, below which the systems become antiferromagnets. The magnetic structure within the *a-b* plane consists of chains of parallel Fe spins that are coupled antiferromagnetically in the orthogonal direction, with an ordered moment typically less than one Bohr magneton. Hence these are itinerant electron magnets, with a spin structure that is consistent with Fermi-surface nesting and a spin wave bandwidth ~200 meV. The rare-earth moments order antiferromagnetically at low T like 'conventional' magnetic-superconductors. With doping, the structural and magnetic transitions are suppressed in favor of superconductivity, with superconducting transition temperatures up to 56 K, while the Ce crystal field linewidths are affected when superconductivity sets in. The application of pressure in $CaFe_2As_2$ transforms the system from a magnetically ordered orthorhombic material to a 'collapsed' non-magnetic tetragonal system which is superconducting at lower T when anisotropic pressure is applied. $Fe_{1+x}Te$ shows a transition from a monoclinic to orthorhombic low T structure with increasing x, and a crossover from commensurate to incommensurate magnetic order. Se doping suppresses the magnetic order, while incommensurate magnetic scattering is observed in the superconducting regime.

INTRODUCTION

The nature of the magnetic order in superconductors has had a rich and interesting history, and has been a special topic of interest ever since the parent materials of the high T_C cuprates were found to be antiferromagnetic Mott insulators that exhibit huge exchange energies within the Cu-O planes. For the newly discovered iron oxypnictide class of superconductors, the observation of long range spin-density-wave-type antiferromagnetic order in the undoped materials has naturally led to strong parallels being drawn between these two classes of materials. Here we provide a very brief review, which by necessity will be restricted to the neutron scattering experiments carried out at the NCNR. We discuss the structure and magnetic transitions of the undoped materials and how these progress with doping into the superconducting regime. We also discuss the spin dynamics for $SrFe_2As_2$, and the search for a possible magnetic resonance in the superconducting state.

DIFFRACTION

Diffraction measurements have been carried out on the undoped La [1,2], Ce [3], Nd [4,5], and PrOFeAs [6] (1:1:1:1) materials, as well as the Ba- [7], Sr-[8], and $CaFe_2As_2$ [9,10]

(1:2:2) systems. The crystal structure consists of single Fe-As layers that are separated by a single layer of (for example) LaO or Ba, respectively. They are all tetragonal at room temperature, but undergo an orthorhombic distortion at lower temperatures. For the 1:2:2 materials the structural transition is first-order in nature, and is directly accompanied by antiferromagnetic order. For the 1:1:1:1 systems the structural component of the ordering also appears to be first order, but the antiferromagnetic order generally develops at a lower temperature and appears to be second order.

The magnetic structure within the *a*-*b* plane is identical for all these materials and consists of chains of parallel Fe spins that are coupled antiferromagnetically in the orthogonal direction, with an ordered moment typically less than one μ_B. Hence these metals are itinerant electron magnets, with a spin structure that is consistent with Fermi-surface nesting, but they also have strong electron correlation effects. Along the *c*-axis the nearest-neighbor spins can be either antiparallel as for the La and Nd 1:1:1:1 systems, or parallel like Ce and Pr. For the related LaOFeP system there is no long range magnetic order [11]. For the 1:2:2 materials, the spins are (also) parallel along the shorter *b*-axis and antiparallel along the longer *a*-axis within the *a*-*b* plane, while along the *c*-axis .nearest neighbors are antiparallel. The spin direction is along the *a*-axis.

For the $CaFe_2As_2$ system, the application of modest pressure (a few kbars) causes a strongly first-order phase transition to a "collapsed" tetragonal phase. By collapsed we mean that there is a huge decrease in the *c*- axis lattice parameter, by 10%, and an overall decrease in the volume of the unit cell by 5%; the *a*-*b* plane undergoes a smaller expansion [9,10]. A region of superconductivity is found in this collapsed phase. However, the initial reports of superconductivity were carried out with a solid medium providing the pressure, before the large changes in the structure were discovered, and because of the huge anisotropic change in the lattice, the pressure applied to produce the superconductivity is also hugely anisotropic. It turns out that under hydrostatic pressure, which is how the diffraction measurements were carried out, the superconductivity is absent. The detailed origin of the superconductivity is now not resolved, but the implications for epitaxial growth of thin films with the appropriate stress is obvious.

For the 1:1:1:1 systems, the rare earth ordering has been studied for the Ce [3], Nd [4], and Pr [6] materials. They all order at low T like "conventional" magnetic superconductors; T_N(Ce) = 4 K, and T_N(Nd) = 2 K. It is interesting, however, that the ordering temperature for Pr is much higher, T_N(Pr) = 14 K, much like what happens in the 1:2:3 cuprate superconductors where T_N(Pr) = 17 K [12].

The doping dependence of the structural and magnetic transitions has been investigated in detail for the La and Ce 1:1:1:1 materials. The structural and magnetic temperatures for both decrease with increasing doping content. The Néel temperature decreases more rapidly than the structural transition, and for the Ce system [3] it is clear that it vanishes before superconductivity appears. Therefore these two order parameters appear to fully compete with each other. For the La 1:1:1:1 system the transition as a function of doping may be first order or there could be coexistence [2], while for the $Ba_{1-x}K_xFe_2As_2$ there is evidence of coexistence of antiferromagnetic order and superconductivity [13]. On the other hand, the orthorhombic structural phase overlaps the superconducting regime, although the optimal T_C appears to occur in the tetragonal phase.

Finally we discuss recent work on the Fe_{1+x}(Te-Se) system [14,15]. Crystallographically there are two iron sites, one of which is partially occupied, while the (Te, Se) site is fully occupied. For the pure Te system the structure is tetragonal at room temperature, but distorts

into a monoclinic structure (for example at 67 K for $Fe_{1.068}Te$ [15]), where commensurate antiferromagnetism abruptly sets in. Both Fe sites are active magnetically, and the nature of the distortion as well as the magnetic structure the system exhibits are different than the 1:1:1:1 and 1:2:2 systems. This contrasts with theoretical expectations based on a 1:1 stoichiometry, but the difference may be due to the additional iron site. Interestingly, at higher Fe content (for example $Fe_{1.141}Te$ [14]) the magnetic order becomes incommensurate, and the incommensurability wave vector is strongly dependent on the Fe content. With Se doping the structural distortion changes from monoclinic to orthorhombic while the magnetic order is suppressed in favor of superconductivity. However, incommensurate spin fluctuations survive into the superconducting regime [14].

SPIN DYNAMICS

Single crystals are available for the 1:2:2 materials (and for the 1:1 systems) that are not only large enough for neutron diffraction studies, but inelastic studies as well. We have measured the low energy spin dynamics in $SrFe_2As_2$ [16]. These data reveal that the in-plane spin dynamics are very energetic, reaching an estimated ~200 meV, and this energy scale is similar to that of the S=1/2 Cu spins in the Mott insulating cuprates. In contrast to the cuprates, though, there is significant spin wave dispersion along the *c*-axis, although the overall dispersion is quite anisotropic. There is also a significant (~6.5 meV) spin gap in the parent material.

Two studies have been carried out on polycrystalline samples to investigate the superconducting properties. A search for a possible magnetic resonance signal in the superconducting state was carried out for $LaO_{0.87}F_{0.13}FeAs$, and an upper bound on any magnetic signal was established [17]. In addition, detailed measurements of the energies and linewidths of the 18 meV Ce crystal field level in superconducting $CeO_{0.84}F_{0.16}FeAs$ were taken [18]. Below the superconducting transition there is a substantial increase in the intrinsic linewidth of the level. When the superconducting gap opens, a decrease in the linewidth would be expected for any excitations below the gap, while an increase would be expected for excitations above the gap due to a 'piling-up' of the available electron states. This linewidth behavior has been observed for phonons in conventional electron-phonon superconductors, and for crystal field levels as well. In the present case the 18 meV level should be above the gap, and hence an increase in the linewidth would be expected, as observed. A dramatic splitting of the crystal field levels was also observed for the undoped system when the magnetic system orders.

FUTURE DIRECTIONS

This is a very young field as far as the superconductivity is concerned, but the pace of research has been extremely rapid. At this point the basic physics of the undoped (parent) 1:1:1:1 and 1:2:2 materials is fairly well established in terms of the structure, magnetic order, and spin dynamics, and in terms of how these overall properties compare with expectations based on first-principles theoretical calculations. Of course, there are many issues still to be resolved. The spin waves need to be measured to higher energies, and determine if there is damping from single-particle (Stoner) excitations as might occur for itinerant electron systems. Much progress also has been made on the doping dependence of the properties, in that it is clear that the structural and magnetic phase transitions are reduced and eventually disappear as the superconductivity develops. It appears that the magnetic order does not overlap with the

superconductivity in some systems, but it apparently does in others. This coexistence could be macroscopic in origin, or it could be intrinsic, and this issue will only be resolved when the question of inhomogeneity is fully addressed; the question is whether these two order parameters are mutually exclusive. It does appear that magnetic fluctuations persist into the superconducting regime, and the elucidation of the magnetic fluctuation spectrum in the superconducting regime is one of the most important areas to explore. The magnetic fluctuations are the present frontrunner among possible pairing mechanisms, as is the case for the cuprates; both systems are highly correlated electron materials—the cuprates more so. However, the pairing mechanism is by no means settled for either system; one only has to recall that the pairing mechanism in the cuprates is still elusive after more than two decades of intensive research. There may be some surprises for the community, and perhaps the iron-based superconductors will provide the key to understanding both classes of materials.

The discovery of high temperature superconductivity in these iron-based materials has focused the attention of the condensed matter physics community on these new superconductors, and although the superconductivity is new, they belong to an enormous class of systems with a wide variety of properties. This will enable the physical properties to be tailored both to investigate the fundamental properties of these systems as well as for applications. This flexibility provides an enormous potential that will stimulate the field for the foreseeable future.

ACKNOWLEDGMENTS

The author thanks all of his co-authors as listed in the references. At the date this paper was written, URLs or links referenced below were deemed to be useful supplementary material to this paper. Neither the author nor the Materials Research Society warrants or assumes liability for the content or availability of URLs referenced in this paper.

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